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# CASSCF AB INITIO STUDIES OF ORGANIC PEROXIDE AND HYDROPEROXIDE FORMATION BY SINGLET OXYGEN ADDITION TO UNSATURATED AND AROMATIC COMPOUNDS

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Singlet-oxygen addition to unsaturated and aromatic compounds plays an important role in the peroxidation processes that occur in living organisms. Many theoretical studies were carried out of the 1,2-addition, but only one MINDO/3-CI and one *ab initio* UMP2 study of oxygen addition to butadiene and one semiemiprical and DFT study of oxygen addition to benzene were reported, but no study was carried out at the MCSCF level. Therefore we devoted our present study to the cycloaddition reactions of the singlet ($^1\Delta_g$) oxygen to *cis*-1,3-budadiene and benzene, respectively, with the formation of 1,2-dioxa-cyclohexene-4 (models of oxygen 1,4-cycloaddition to conjugated compounds) by means of the CASSCF/MCDQPT2 *ab initio* method with the 6-31G* basis set. In the case of butadiene the reaction is exoenergetic and the product has a $C_2$ symmetry, with the peroxide moiety in the *gauche* configuration. In the case of benzene the reaction is endoenergetic and the tricyclic product formed has a $C_{2v}$ symmetry with the peroxide moiety in the *syn* configuration. Three possible reaction routes were studied: i) concerted cycloaddition, ii) two-stage cycloaddition with the formation of a five-membered ring peroxirane intermediate, and iii) two-stage cycloaddition with the formation of a linear intermediate. In the case of butadiene routes i) and ii) were excluded, because only second-order saddle points were found on the corresponding reaction pathways. The linear intermediate (I1) found on route iii) has a biradicaloid character and its relative energy is 4.09 kcal/mol, taking into account the basis set superposition error (BSSE). The dominant activation barrier corresponds to the transition state TS1 leading to I1 and amounts to 13.5 kcal/mol. The rearrangement of I1 to the product (P) involves only a minor activation barrier of 3.5 kcal/mol (relative to I1). In the case of benzene the concerted binding mode is favored, the activation barrier being 25.25 kcal/mol. This difference in binding mechanism can be explained in terms of the configuration of peroxide moiety in the adduct.

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